SEMI-ANNUAL PROGRESS REPORT N72-28278

on

I. Nonequilibrium Shock-Wave Structure

II. Kinetices of Nitric Oxide Formation and Decomposition

for the period

November 1, 1971 - June 1, 1972

submitted to the

National Aeronautics and Space Administration

Washington, D. C.

submitted by

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NASA Grant NGR-05-020-583

1. INTRODUCTION

This is a progress report of work carried out during the first six months of support under NASA Grant NGR-05-020-583. As proposed, we have utilixed this initial period to survey the available literature and to select and design meaningful experiments for the two subject areas of the grant. Our suggestions for experimental work together with some supporting calculations are described briefly in the following two sections.

2. NONEQUILIBRIUM SHOCK-WAVE STRUCTURE

Important progress is being made at Ames Research Center and elsewhere in the development of molecular flow simulation methods. In brief, the concept is to simulate real gas flows using a computer and a sample of model molecules or atoms which are allowed to undergo collisions with each other in a manner representative of actual molecules or atoms.

The emphasis of the work at Ames has been placed on the theoretical and numerical aspects of flow simulation, although in each stage of the simulation development experimental data from various laboratory experiments have played an important role in corroborating the computational techniques and the intermolecular collision models employed. For example, in the first stage of simulation development interest was focussed on modeling steady one-dimensional flows of inert gases, and experimental data on the structure of normal shock waves (obtained at Caltech) were used to establish the proper intermolecular potentials for the inert gas atoms and also to verify the numerical techniques in the simulation. More recently, attention was directed toward the simulation of flows in which an inert gas intereacts strongly with a bounding surface, and we performed shock-tube experiments on the reflection of planar shock waves from a coplanar surface to provide the data needed to establish a reasonable gas-surface collision model. We were also able to use these experimental data as a test of the

simulation accuracy for non-steady one-dimensional flows. Part of that work was performed under support of the present grant and the results will be presented* at the forthcoming International Rarefied Gas Dynamics Symposium.

Current activity in the field of flow-simulation research at Ames is concerned with the development of collision models for diatomic and triatomic gases undergoing rotational excitation and energy exchange. Our survey has shown that experimental data needed for the development and testing of these collision models are particularly lacking, especially at conditions representative of reasonable flow processes. Experiments to provide such data are difficult, firstly because controlled nonequilibrium must be induced between the rotational and translational energy modes, and secondly because one needs to monitor the rate at which the rotational energy distribution readjusts, and in particular to monitor the rates at which energy flows in and out of specific rotational quantum levels. The remainder of this section will deal with the new experiment we propose to provide such rotational relaxation data.

The experiment we propose, should NASA agree to support further work in this area, is the measurement of the nonequilibrium rotational energy distribution within a shock wave in a molecular gas. The experiment would be performed in a shock tube and the diagnostic technique would be tunable infrared laser absorption in the fundamental vibration-rotation band of the species under study. The results of the measurements would be time-dependent population histories of individual rotational levels (in the ground vibrational and electronic state of the molecules) during passage of the shock wave. Such results could be compared with simulation predictions for the same nonequilibrium flow process based on simple

*G. Deiwert and R. Hanson, "The Reflection of a Planar Shock Wave from a Coplanar Surface," to be presented at the Eight International Rarefied Gas Dynamics Symposium, Palo Alto, California, July 1972.

molecular collision models with a reasonable number of unknown and adjustable parameters. Selection of proper values for these parameters would complete the collision models and allow their use in the simulation of other more practical flows of molecular gases.

Energy exchange between rotational and translational energy modes is most conveniently studied in the absence of changes in the vibrational energy distribution. The structure of a normal shock wave in a molecular gas is ideal for this purpose since rotational relaxation is complete before vibrational relaxation begins. That is, during the initial portion of the shock wave, the translational and rotational energy modes will adjust to new equilibrium distributions while essentially all of the molecules remain frozen in the lowest vibrational energy level.

One way of monitoring the time-dependent concentrations in the various rotational quantum levels is by absorption of monochromatic infrared radiation at the fundamental vibration-rotation band frequencies corresponding to transitions $(\nu = 0, J) \rightarrow (\nu = 1, J \pm 1)$. We feel that recently developed simiconductor lasers, together with high-speed infrared detectors, offer exciting new posibilities for this purpose. Measured variations in the absorptivity across the shock tube, together with a knowledge of the absorption coefficient could thus be used to infer the variations in number density $n_J(t)$ in the level $(\nu = 0, J)$. Approximate calculations illustrating the feasibility of this new approach form the remainder of this section.

For unidirectional light, of intensity I_ν at frequency ν, the absorption coefficient per unit length is defined as

$$\alpha\ (\nu),\ \mathrm{cm}^{-1} = -(1/I_\nu)(dI_\nu/dx)$$

Neglecting spontaneous and induced emission (valid approximations for the proposed shock-structure experiments) this absorption coefficient is simply related

to the Einstein coefficient for induced absorption, $B_{\ell u}$, and the number density of absorbers, N_ℓ, i.e.,

$$\alpha(\nu) = \frac{h\nu}{4\pi} \phi(\nu) B_{\ell u} N_\ell .$$

$\phi(\nu)$ is the line-shape function. We anticipate that the lines will be Doppler broadened and that the laser will be tuned to line center so that the appropriate shape function is

$$\phi(\nu_o) = \lambda_{u\ell} (m/2\pi kT)^{1/2}$$

where m is the molecular mass, $\lambda_{u\ell}$ is the laser wavelength and T is the translational temperature. Simple (and approximate) recursion relations exist between the Einstein coefficients for different vibration-rotation transitions; for the transitions of interest between ν=0 and ν=1 the relations are

$$B_{\ell u} = \frac{\bar{B}_{01} J}{2J+1} , \text{ P branch } (\Delta J = -1)$$

and

$$B_{\ell u} = \frac{\bar{B}_{01} (J+1)}{2J+1} , \text{ R branch } (\Delta J = +1)$$

where J is the rotational quantum number of the lower level and $\bar{B}_{01}$ is a constant (essentially the Einstein coefficient for a rotationless transition between ν=0 and ν=1).

For purposes of illustration, we present calculations for CO ($\bar{B}_{01} \simeq 8.5 \times 10^6$ sec/gm) and P-branch transitions. Results for other diatomic gases and many triatomic gases would be similar. If we assume that all the molecules remain in the lowest vibrational level, ν=0, and that the rotational and translational energy modes are in equilibrium at temperature T, then the absorption coefficient at line center reduces to

$$\alpha/P, \text{ cm}^{-1}\text{-torr}^{-1} = \frac{8.4 \times 10^5}{T^{5/2}} J \exp - \frac{\Theta_r}{T} J(J+1)$$

The quantity Θ_r is the characteristic rotational temperature equal to 2.78°K for CO. The thermal equation of state, P = NkT, has been used in order to express the absorption coefficient in terms of the partial pressure of CO. A plot of this absorption coefficient versus temperature is shown in Fig. 1 for selected values of J. The first conclusion to be drawn is that the absorption coefficient is strongly dependent on both temperature and pressure. We can now utilize these curves to estimate the sensitivity of the laser absorption to changes in the rotational distribution through a shock wave.

In the experiment we would measure the change in the transmitted light intensity as function of time through the shock wave, i.e., I(t) - I(t=0). We can estimate the sensitivity of our proposed technique by considering the total change in transmitted intensity across the shock wave, i.e., $I(t\to\infty)$ - I(t=0). Now $I(t\to\infty)$ is determined by the equilibrium (rotational and translational) conditions behind the shock wave, i.e. $I(T_2, P_2)$ where T_2 and P_2 are given by the Rankine-Hugoniot equations; I(t=0) is determined by the initial shock-tube conditions, i.e. $I(T_1, P_1)$. The overall change in transmitted intensity is

$$\Delta I = I(T_2, P_2) - I(T_1, P_1) = I_o(e^{-\alpha_2 L} - e^{-\alpha_1 L})$$

or, in normalized form,

$$\Delta I/I_o = e^{-\alpha_2 L} - e^{-\alpha_1 L}$$

where L is the optical path length across the shock tube and I_o is the (constant) laser intensity prior to passage across the shock tube. We can obtain typical values for the change in intensity using the curves in Fig. 1 and values for the shock-wave temperatures and pressures. Reasonable initial conditions would be P_1 = 0.1 torr CO and T_1 = 300°K. The quantities P_2 and T_2 are strong functions of the shock Mach number which may be varied over wide limits. As an example, we chose Mach = 5, so P_2 = 2.9 torr and T_2 = 1740°K. Table I shows the overall

change in transmitted intensity for selected rotational quantum numbers and these shock conditions. A value of L = 3 cm was used in the calculations. (A short absorbing path length L in a large-diamter shock tube is necessary for shock-wave structure experiments in order to maintain good spatial resolution in the presence of significant shock-wave curvature.) The results in Table I show that significant changes in transmitted intensity (generally greater than 10%) may be expected for all the important quantum levels.

J	α_1	α_2	I_1/I_o	I_2/I_o	$\Delta I/I_o$
1	.053	.011	.853	.967	+ .114
5	.200	.094	.550	.754	+ .196
9	.210	.150	.533	.638	+ .105
13	.130	.190	.677	.566	- .111
17	.055	.205	.848	.541	- .307
21	.016	.200	.953	.549	- .404
25	.013	.170	.991	.601	- .390
29	.0005	.135	.999	.667	- .332
39	10^{-6}	.061	1	.832	- .168

TABLE I. Mach = 5, P_1 = 0.1 torr CO

The calculations made here are admittedly crude, in the sense that the rotational nonequilibrium which exists between conditions 1 and 2 was not considered, but the results are adequate to conclude that the laser-absorption technique is a sufficiently sensitive method for measuring rotational populations in a nonequilibrium shock wave. More-detailed calculations, still in progress, substantiate this conclusion.

It was originally planned that AMES would provide the semiconductor for this work. If funds are made available for the purchase of this laser, then the next step in our research on molecular-gas collision models will be to

conduct shock-tube experiments. Independent of that decision, our work to develop a simulation model for gas-surface interaction is nearing its final stages, and we hope to complete this work and submit it for journal publication within the next six months or so.

3. KINETICS OF NITRIC OXIDE FORMATION AND DECOMPOSITION

Increasing awareness of the fundamental role of gaseous nitric oxide (NO) in atmospheric pollution has established the need for a more complete and de-dailed understanding of NO kinetics than currently exists. For example, the NO currently introduced into the atmosphere by power generation stations and aircraft and automobile engines, and also the NO which will be emitted by future supersonic transport and space shuttle flights, depends on the finite rates of chemical reactions which form and decompose NO. During the first six months of our work on this topic, we have surveyed the available literature on NO chemical rate data and concluded that further experiments are seriously needed to reduce the significant uncertainties which exist in several of the key re-action rates. In fact, in the case of NO decomposition reactions, there are still important questions regarding the proper reactions paths. In the remainder of this section, we will outline the experiments we propose to provide the needed rate-constant information.

The experiments will be performed in a shock tube because the temperatures of interest cannot be achieved in static systems. In the case of NO formation, we will shock heat various N_2-O_2 mixtures and monitor the rate of formation of NO over a range of temperature and pressure. The mechanism for NO formation in suddenly heated air is known to begin with the dissociation of O_2,

$$O_2 + M \rightarrow 2O + M \qquad (1)$$

followed by the fast Zel'dovich exchange reactions

$$O + N_2 \rightleftarrows NO + N \qquad (2)$$

$$N + O_2 \rightleftarrows NO + O \qquad (3)$$

where M is a general collision partner; k_1 and K_{-1} are the forward and reverse rate constants for reaction (1), etc. The dissociation rate k_1 is reasonably well known, so attention will be directed toward measurement of k_2 and k_3. Experimentally, we propose to monitor the density gradient in the gas using a laser schlieren system; in addition, the NO concentration will be monitored using infrared emission from the fundamental vibration-rotation band at 5.3 microns. The experiments will be performed behind both incident and reflected shock waves, and the rate constants will be inferred through comparison of measured results and calculations based on hypothesized and known rate constants coupled with the conservation equations of gas dynamics. An alternate technique for measuring the NO concentration behind shock waves would be ultraviolet absorption in the NO γ-bands.

The decomposition of NO in nitrogen-oxygen systems is still poorly understood. The principal reactions are generally taken to be

$$NO + NO \rightarrow N_2O + O \qquad (4)$$

$$NO + M \rightarrow N + O + M \qquad (5)$$

$$NO + NO \rightarrow N_2 + O_2 \qquad (6)$$

$$N_2O + M \rightleftarrows N_2 + O + M \qquad (7)$$

$$O + NO \rightleftarrows N + O_2 \qquad (8)$$

$$N + NO \rightleftarrows O + N_2 \qquad (9)$$

The reaction path for suddenly heated NO is probably reactions 4, 5 and 6 in parallel followed by the decomposition reaction 7, if reaction 4 is truly important, and the fast Zel'dovich reactions 8 and 9. The most recent views on reaction 6 are generally that it may be neglected compared with the importance of

reactions 4 and 5. We propose to infer k_4 and k_5 by separately monitoring NO, N_2O and O concentrations behind shock waves in NO and NO-Ar systems. Our diagnostics will include infrared emission at 5.3 and 4.6 microns to determine the NO and N_2O concentrations, respectively, and NO chemiluminescence ($NO + O \rightarrow NO_2 + h\nu$) to determine the O-atom concentration. We will also utilize a laser-schlieren system to monitor the density gradient in the shock-wave relaxation zone. Reactions 8 and 9 become dominant (rate-limiting) in NO decomposition after sufficient O atoms are generated by reactions 4, 5 and 7. We propose to infer k_8 and k_9 during the latter portions of relaxation zones in shock-heated NO, NO-Ar and NO-O-Ar mixtures. As with the NO formation work, we expect that computer calculations of the relaxation zone using hypothesized or known rate constants will play an important role in our data reduction.

The experiments outlined in this section are still in the planning stages but we anticipate that laboratory work will be initiated in the near future and that we will have more specific results available by the time of the next progress report.

4. CONCLUDING REMARKS

Recent reorganizations at Ames Research Center may influence the future emphasis of our research. Originally our work was planned to support the activities of the Physics Branch at Ames, but that branch has recently been disbanded. With some minor changes in emphasis, we expect that our work will provide useful support for research being carried out in the Thermo- and Gas-Dynamics Division at Ames. Accordingly, we suggest that C.F. Hansen, Chief of the Physical Gas Dynamics and Lasers Branch, in the Thermo-and Gas-Dynamics Division, act as the future technical monitor of our research.

These reorganizations have also raised an important question regarding the

purchase of the semiconductor laser needed for the shock-wave structure experiments, and until a decision is reached regarding Ames' purchase of that laser our work on shock structure is uncertain.

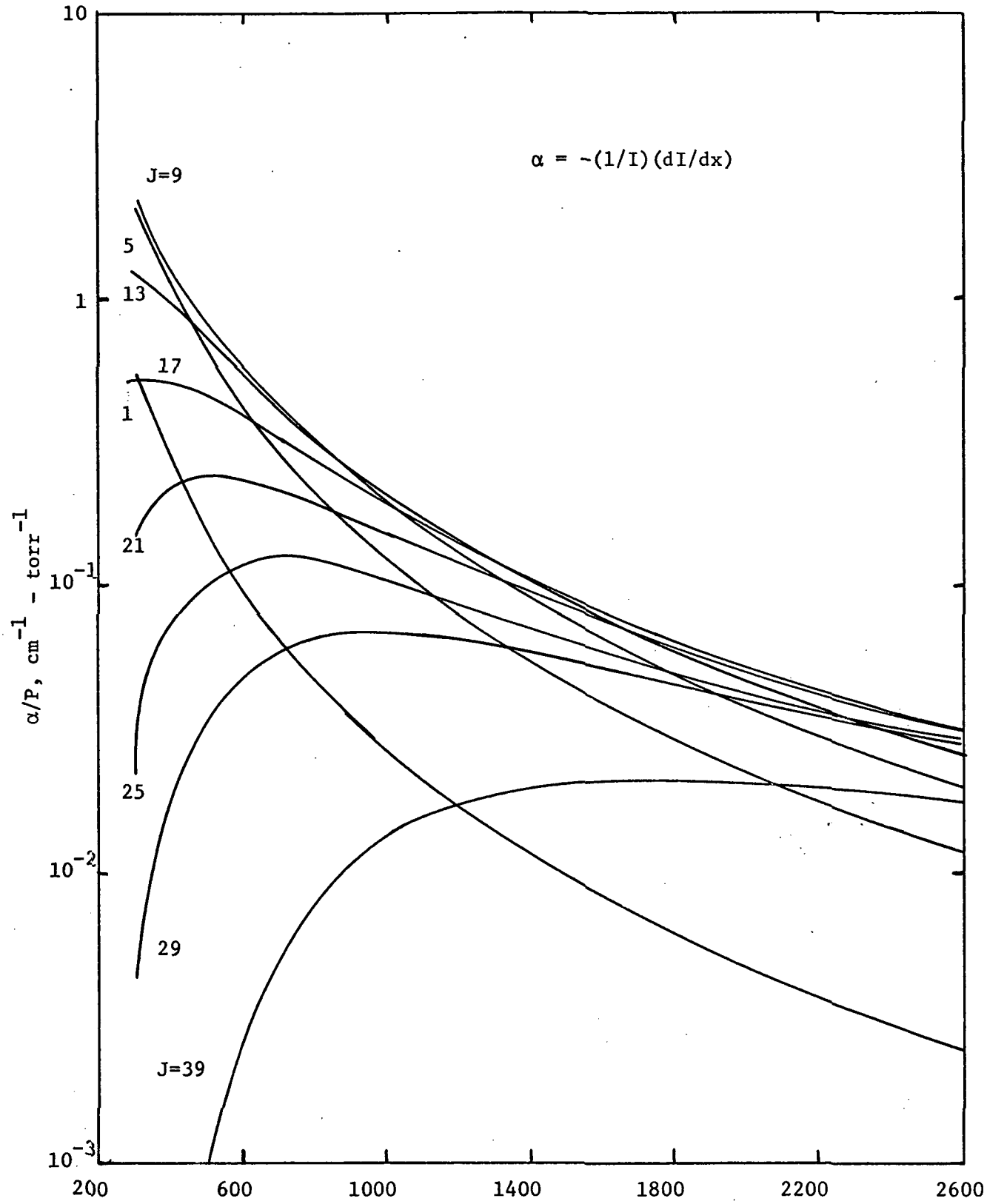

FIG. 1 P-branch absorpiton coefficient at line center in CO: T_{vib} = 300°K; ν, $J \rightarrow \nu+1$, $J-1$ with $\nu=0$.